TITLE: Metal Sulfite/Sulfate Reactions in Thermochemical Hydrogen Cycles*

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SUBMITTED TO: To be presented and included in the Proceedings of the 3rd I.E.A Thermochemical Hydrogen Workshop held at the Tsukuba Center for Science and Technology, Japan, June 18-21, 1980.
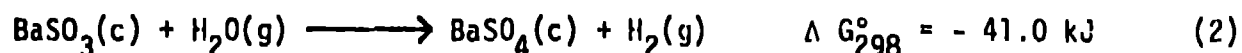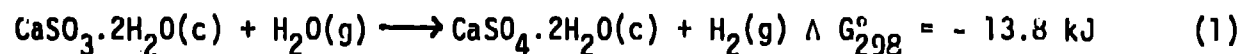
Metal Sulfite/Sulfate Reactions in Thermochemical Hydrogen Cycles*
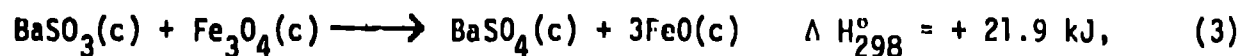
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The thermochemical cycles which have been most extensively developed at this time[1,2,3] all involve the thermal decomposition of sulfuric acid which is corrosive. Metal sulfate cycles have been studied[4,5] as a means of circumventing handling corrosive mixtures at high temperatures. However, these metal sulfate cycles still use an electrochemical step to produce H_2. This abstract examines alternate H_2 producing steps to be used in conjunction with metal sulfates.

The simplest example of such a reaction involves direct oxidation of a metal sulfite by water:

$$CaSO_3 \cdot 2H_2O(c) + H_2O(g) \longrightarrow CaSO_4 \cdot 2H_2O(c) + H_2(g) \quad \Delta G^o_{298} = -13.8 \text{ kJ} \qquad (1)$$

$$BaSO_3(c) + H_2O(g) \longrightarrow BaSO_4(c) + H_2(g) \quad \Delta G^o_{298} = -41.0 \text{ kJ} \qquad (2)$$

However, although conceptually possible, when experimentally investigated[6] no reaction was obtained. A modification was tried using magnetite:

$$BaSO_3(c) + Fe_3O_4(c) \longrightarrow BaSO_4(c) + 3FeO(c) \quad \Delta H^o_{298} = +21.9 \text{ kJ}, \qquad (3)$$
$$\Delta G^o_o - 540 \text{ K}$$

$$3FeO(c) + H_2O(g) \longrightarrow Fe_3O_4(c) + H_2(g) \quad \Delta G^o_{298} = -52.7 \text{ kJ} \qquad (4)$$
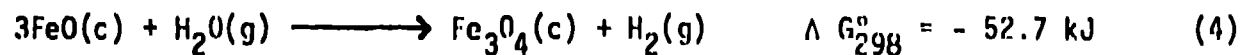
Again, no reaction was observed.

Another type of sulfite oxidation, for which experimental proof has been obtained, utilizes I_2:

$$MSO_3(c) + MgO(c) + I_2(c) \xrightarrow{H_2O} MSO_4(c) + MgI_2(aq) \qquad (5)$$

$$\text{where } M = Mg, \; \Delta H^\circ_{298} = -333.1 \text{ kJ} \qquad (5a)$$

$$M = Ca, \; \Delta H^\circ_{298} = -255.7 \text{ kJ} \qquad (5b)$$

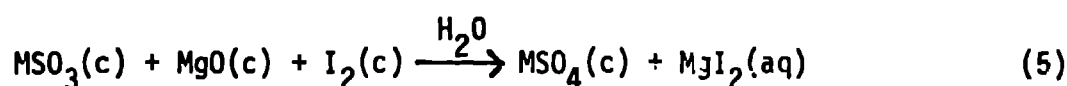$$M = Ba, \; \Delta H^\circ_{298} = -265.7 \text{ kJ} \qquad (5c)$$

when M = Ca or Ba, product separation is trivial since their sulfates are insoluble. However, $MgSO_4$ is soluble so for reaction (5a) the problem of separating sulfate and iodide remains. Drying, hydrolysing MgI_2 and thermally decomposing the resultant HI replaces the electrochemical and drying steps in the Westinghouse cycle. Drying and hydrolysing MgI_2 replaces drying and separating HI in the GA cycle. Experimentally, when using dilute solution (0.2 mol 1^{-1}) at room temperature all these reactions proceed rapidly and are probably complete within the first minute of mixing (as evidenced from the color change from a grey suspension to a white suspension and brown solution). They have all been shown to be complete within 1 h (> 95%). In case (5a) a brown solution is formed since $MgSO_4$ is soluble. In the Ca case, the reaction was repeated using the half hydrate at higher concentration. At 2.0 mol 1^{-1} ($H_2O/CaSO_3 = 28$), the reaction was complete, whereas at 4.0 mol 1^{-1} ($H_2O/CaSO_3 = 14$) 73% of the reaction took place. This relatively low yield was due both to the exothermicity which caused some of the I_2 to vaporize and also to the mud-like nature of the reactants which made stiring difficult.

The cycle is completed by thermally decomposing the sulfate (as well as hydrolysing MgI_2 and thermally decomposing the resultant HI). Both Ba and Ca sulfates decompose above the temperature range often considered available for tch cycles:

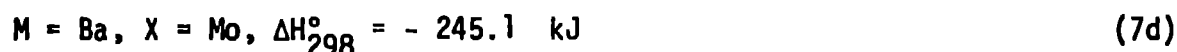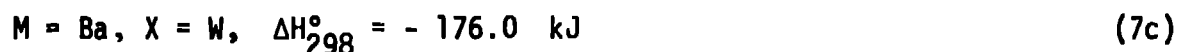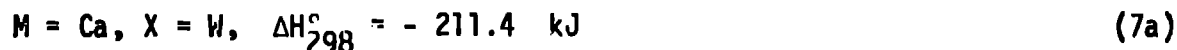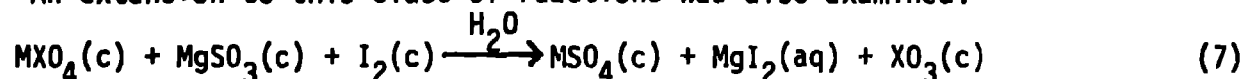$$MSO_4(c) \longrightarrow MO(c) + SO_2(g) + 1/2 \, O_2(g) \qquad (6)$$
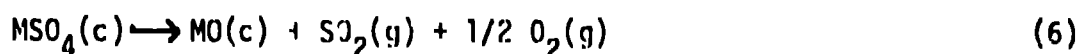
$$\text{where } M = Mg, \; \Delta G^\circ_{1170} = 0 \qquad (6a)$$

$$M = Ca, \; \Delta G^\circ_{1810} = 0 \qquad (6b)$$

$$M = Ba, \; \Delta G^\circ_{2030} = 0 \qquad (6c)$$

Conceptually, however, an insoluble sulfate with a lower decomposition temperature can be used.

An extension to this class of reactions was also examined:

$$MXO_4(c) + MgSO_3(c) + I_2(c) \xrightarrow{H_2O} MSO_4(c) + MgI_2(aq) + XO_3(c) \tag{7}$$

$$M = Ca, \ X = W, \quad \Delta H^\circ_{298} = -211.4 \ \text{kJ} \tag{7a}$$

$$M = Ca, \ X = Mo, \ \Delta H^\circ_{298} = -221.2 \ \text{kJ} \tag{7b}$$

$$M = Ba, \ X = W, \quad \Delta H^\circ_{298} = -176.0 \ \text{kJ} \tag{7c}$$

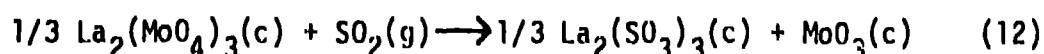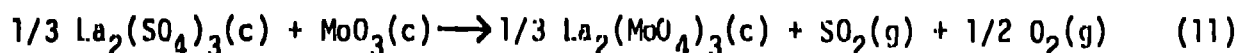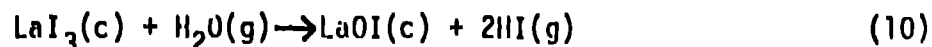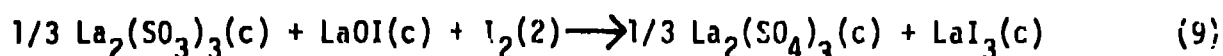$$M = Ba, \ X = Mo, \ \Delta H^\circ_{298} = -245.1 \ \text{kJ} \tag{7d}$$

The advantages of these reactions is that the oxide lowers the decomposition temperature of the sulfate:[7]

$$MSO_4(c) + XO_3(c) \longrightarrow MXO_4(c) + SO_2(g) + 1/2 \ O_2(g) \tag{8}$$
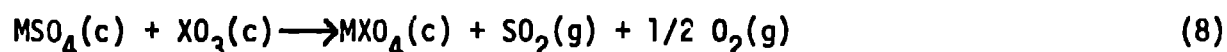
The observed course of reaction (7a) in dilute solution (0.2 mol l^{-1}) leaves $CaWO_4$ unchanged but converts all the I_2 to iodide. Some SO_2 is evolved. Reactions (7b,c,d) occur as written, Ca(or Ba)SO_4 is precipitated and all the I_2 is converted to iodide. No oxide has been seen in the x-ray powder diffraction pattern of the solid product, but the weights obtained suggest it is present. Reactions (7b,c,d) were also carried out in acetone in order to cut down the heat of vaporization of the solvent (+30.5 kJ mol^{-1} vs. + 43.9 kJ mol^{-1} for water). However, in all cases, MXO_4 was recovered unchanged at the end of the reaction time (0.5 h). In an allied concentrated aqueous reaction using $BaWO_4$ and $MgSO_3$ (2.9 mol l^{-1}), $BaWO_4$ was recovered unchanged although $MgSO_3$ was completely converted to sulfate. Note that in dilute aqueous solution (0.2 mol l^{-1}), $BaWO_4$ was completely converted to $BaSO_4$ and WO_3.

This work is being extended to include a similar cycle based on lanthanum:

$$1/3 \ La_2(SO_3)_3(c) + LaOI(c) + I_2(\ell) \longrightarrow 1/3 \ La_2(SO_4)_3(c) + LaI_3(c) \tag{9}$$

$$LaI_3(c) + H_2O(g) \longrightarrow LaOI(c) + 2HI(g) \tag{10}$$

$$1/3 \ La_2(SO_4)_3(c) + MoO_3(c) \longrightarrow 1/3 \ La_2(MoO_4)_3(c) + SO_2(g) + 1/2 \ O_2(g) \tag{11}$$

$$1/3 \ La_2(MoO_4)_3(c) + SO_2(g) \longrightarrow 1/3 \ La_2(SO_3)_3(c) + MoO_3(c) \tag{12}$$

Unlike reaction (5), reaction (9) is thermodynamically possible in the absence of water. In order to effect a separation of the products, however, a solvent for one of the products must be used. $La_2(SO_4)_3$ is insoluble in water (especially at elevated temperatures) while LaI_3 is soluble. $La_2(SO_4)_3$ is also insoluble in acetone. Acetone, not only requires less energy for vaporization than water, it also, by allowing the reaction to be carried out in the absence of water, prevents the formation of hydrates.

Reaction (11) has been studied[7] and reasonable rates are obtained at 1075K. $La_2(SO_4)_3$, itself, decomposes at 1270 K.[8]

References

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6. C. F. V. Mason, Unpublished Results (1979).

7. C. M. Hollabaugh, T. C. Wallace, M. G. Bowman, and W. M. Jones, Proc. 3rd World H_2 Energy Conference, Tokyo (1980).

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